Spontaneous Luminescence of Coal During Dehydration

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Introduction

Triboluminescence (TL) is the emission of light which occurs when a solid is subjected to some form of "stress." Although the phenomenon was named for the Greek root for the verb "to rub"(1), it is now known that mechanical action other than grinding, scrapping or rubbing will initiate triboluminescence. It has been observed that static electrification, exposure to light, the motion of a fluid (most notably mercury) over the surface, thermal shock and the release of absorbed or adsorbed gases can provide sufficient energy to induce TL in a solid (2). Furthermore, although light emission has been associated largely with organic crystalline materials, recent research has shown that some rock minerals also display triboluminescent properties (3,4).

It has been reported that TL is frequently observed to occur in materials which also give rise to a photoluminescence (PL) spectrum, but PL is not a necessary characteristic for TL behavior (2). There is an extensive body of literature on the subject of TL, but to date neither the exact origin(s) nor the mechanism(s) of TL have been delineated precisely. Investigators have most commonly studied the role of crystal fractures, plastic and elastic deformations, particle size, the presence or alteration of crystal defects, and/or the presence of impurities for their potential relationship to TL (6).

Coyne et al. were the first to report that dehydration of some clay minerals results in triboluminescence (4). That work also revealed that in addition to a burst of photons, a continued release of measurable energy was recorded for periods of time as long as several days (4,5).

Coyne's work prompted us to investigate TL properties in coal in spite of its non-crystalline structure. Coal is frequently underlain with clay beds and clay minerals are the most common inorganic components in coal. Because coal is a complex and a notoriously variable substrate, it was desirable to test its luminescent properties under the simplest of conditions. Coyne's work has shown that dehydration causes sufficient "stress" upon the clay structure to stimulate TL, and is a process that can easily be achieved using a common desiccant (4). Since the porous coal structure makes it possible for liquids to be imbibed into the pores as well as to adhere to the surface of the macromolecule, it was decided to monitor TL from coal when water was removed from coal previously suspended in water in a manner analogous to that described by Coyne (4). The primary focus of this study, then, was to determine whether TL could be observed in coal when moisture was removed from it, and whether any photon emission observed could be related to the mineral matter content of the coal. As far as is known, this report marks the first discovery that coal, a complex but clearly an amorphous solid, does exhibit pronounced triboluminescence when an aqueous slurry is subjected to dehydration. In addition to studying the effects of mineral matter content on coal TL, this report includes data on the effect of particle size on coal triboluminescence.

EXPERIMENTAL

Preparation of Aqueous Coal Slurries

Two coals have been used throughout this study. Both are Western Kentucky hvB coals obtained from the Western Kentucky University Center for Coal Science. A summary of the analysis of both coals is given in Table I. It should be noted that these two coals were selected because of the wide divergence in the ash content which is represented.

In the initial series of trials to determine TL, -60 mesh coal was mixed (20% by weight) with water and micronized in a Union Process Model 1-S stirred ball attritor mill for 2 hours. For determinations of the effect of particle size on TL, 120 g of -60 mesh coal #85098 (high ash) and 480 g water were placed in the attritor mill. The micronization process was timed, and at pre-determined intervals the rabble arm was stopped long enough to withdraw approximately 5 mL of the coal-water slurry. Table II summarizes the particle size reduction with milling time for such a slurry. Particle size determinations were made using a Spectrex SP-410 particle size analyzer.

Table II

Particle Size Reduction with Short-term Milling of Coal #86024*

Milling time, min.	% +325 mesh	% -325 mesh
0	12.3	39.0
.5	13.0	58.8
1	17.9	69.2
2	11.0	86.7
4	2.6	97.1

* Coal #86024 is a hvBb coal similar to the #82089 used in this work (7).

Measurement of Triboluminescence

Triboluminescence of the coal was measured as a function of desiccation with time. Photon output was monitored using a Beckman LS-100SC liquid scintillation counter operating in the total photon mode with a 50 - 1,000 window on the discriminator, and full gain. Data was registered as counts per minute and was printed on a paper tape at pre-set intervals. Typically, data was collected at 0.5 min intervals for 2 minutes and at 1 min intervals thereafter for periods as long as 700 min. The coal slurry was applied as a uniform coating about 2.5 cm high around the center of the inside of a standard glass liquid scintillation vial. Blue ("indicating") $CaSO_4$ was poured into the vial to a depth of about 1 cm before applying the coal slurry. The amount of sample applied to the vial was determined directly by weighing. The total sample weight ranged from 60 - 200 mg, or from 12 - 40 mg coal. The vial containing the sample and desiccant was capped and wiped with a damp tissue before being placed in the counting well. The determination of background activity and the photon emission of the coal slurry in the absence of the desiccant was determined by omitting the coal, the desiccant, or both, from the vial before monitoring the photon emission.

RESULTS AND DISCUSSION

Figure 1 shows a portion of the photon output for the #82089 low ash coal which had been micronized for 2 hours (mean particle size about 5 microns) and was then dehydrated with $CaSO_4$ in a closed scintillation vial. Figure 2 shows two additional trials for the same coal using different sample sizes. It is apparent from the recorded counts per minute that triboluminescence does occur in this coal upon dehydration. These graphs show that the intensity of the maximum luminescence is not as sensitive to the size of the sample as the time of drying before on-set of the emission is. For the 87 mg and the 101 mg samples a small emission occurs at 22 and 37.5 min, respectively, followed by a larger and a more gradually decaying

emission maximum at 60 and 69.5 min, respectively. For the 164 mg sample, only one emission peak was observed and it did not occur until an elapsed drying time of 105.5 min. The background, which is not shown on the graphs, was 7,200 +/- 200 cpm throughout the period monitored.

The significance of the apparent delay in the appearance of the emission is not certain at this time. The time plotted on the graphs has not been corrected for the time which elapsed from the preparation of the sample to initiation of counting. However, this did not vary from sample to sample by more than 2 - 3 minutes and clearly does not account for the differences observed for these samples. With increased sample size there is, of course, more total water present. The moisture content at peak emission could not be determined for these samples. An alternative sample configuration, in which the desiccant is held in the center of the vial in a tube punctured with holes, will be tested. It is believed that such a configuration may dry the coal more uniformly and will permit the desiccant to be removed and weighed at any time. It will then be possible also to monitor the change in weight of the desiccant and of the sample, permitting a correlation to be made between the moisture content and photon emission.

The decrease in the intensity of light released was expected to decrease as the film thickness was increased because of increased self-absorption or increased scattering. The data shows that this does occur.

Figure 3 shows a similar pattern of decreased intensity and a longer time before the onset of the photon emission with increasing sample size for the # 85098 high ash coal. When the same sample size (87 mg) was used for both coals, the intensity of the first emission peak is substantially larger in the high ash sample, while the intensity of the second emission peak is nearly the same for both coals. Coyne reported that multiple peaks were frequently observed in TL measurements on kaolinites, but appeared to be only artifacts from non-uniform sample application or variation in particle size distribution (4). There is no justification at this time for discounting the smaller emission peak observed for these coals, however. Because of the heterogeneous nature of coal, the possibility does exist that TL related to organic constituents, or adsorbed gases, as well as to inorganic components is being observed, or that TL related to more than one of the mineral constituents is giving rise to a second emission signal. Additional data are needed to rule out any of these possibilities and to draw a definite correlation between the first emission peak and the ash content of the coal.

Table III summarizes the data from samples obtained by withdrawing aliquots from the attritor mill at timed intervals.

Table III

Effect of Milling on Duration & Intensity of Luminescence of High Ash Coal

Milling time, min.	Sample Wt., mg	Area under peak	Duration of peak, min. (time to max.)	CPM at max.
8	99	82	63 (31)	22,490
16	99	81	32 (42)	20,110
32	80	68	39 (30)	24,180
64	80	43	28 (18)	25,400
128	125	17	22 (20)	13,420

There does not appear to be any direct correlation between the total milling time and either the time of onset of the light emission or the intensity of the light released at the peak maxima. It is apparent, however, that the overall duration of the emission is related to some property of the coal affected by the milling time. Our original hypothesis was that the dehydration was initiating TL by permitting

some "relaxation" in the coal structure, perhaps pore shrinkage, and that TL would be maximized at some critical particle size. Table II shows that after 4 minutes milling time virtually all of the coal has been reduced to -325 mesh (less than 5 microns). Thus, particle size alone can not be giving rise to the photon emission pattern recorded for these samples. The most unexpected observation about the effect of milling on coal is the alteration of its apparent density with extended milling. It was reported that after 4 minutes milling more than 50% of the coal sinks in a 1.3 specic gravity media (7). The discussion and the explanation for these observations is the subject of another study being carried out at Western Kentucky University. For this investigation, it is clear that the observed TL behavior is not related to the internal pore structure, which is rapidly compressed and almost completely destroyed by milling longer than 15 minutes (7).

CONCLUSIONS

To date this study has shown that coal exhibits triboluminescent behavior when an aqueous slurry is subjected to dehydration. The luminescence data is complex. Both the high ash and the low ash coal exhibited a delayed burst of photons. In some cases only one emission maximum was observed which continued to decay monotonically for several hours. The time and the intensity of the emission were related to the sample size, and may be attributed to the total moisture content. In other cases, two distinct emission events were observed. Both peaks were affected by the sample size. Although it has been reported that extended milling effectively destroys the pore structure, triboluminescence is not eliminated when the coal is micronized. This suggests that the observed TL is a surface phenomenon rather than one related to alteration of the pore structure. No clear correlation can be made regarding the effect of ash content on triboluminescence in coal. Work in progress will address both the effect of ash content and the effect of variations in moisture content on TL behavior in more detail. The determination of the wavelenght(s) of photons emitted will also be attempted.

REFERENCES

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Table 1

Characterization of Coals

I.D.*	82089	85098
Seam/ County	Butler Co.	KY #11/Muhlenburg Co.
Proximate		
Moisture**	5.8	4.31
Ash	3.17	18.96
Volatile matter	45.25	34.72
Fixed carbon	51.57	46.30
Ultimate		
Carbon	79.09	63.22
Hydrogen	5.73	4.35
Nitrogen	1.6	1.28
Sulfur	1.08	5.96
Oxygen(diff.)	9.3	6.19
Apparent rank***	hvB-B	hvB-A
Major Inorganics		
SiO_2	--	19.93
CaO	--	2.76
Fe_2O_3	--	32.42
MgO	--	1.51
K_2O	--	1.13
P_2O_5	--	7.8
Al_2O_3	--	(33-est.)

* Accession, WKU Center for Coal Science

** Moisture as-determined; other values reported on dry basis

*** Using as-determined moisture

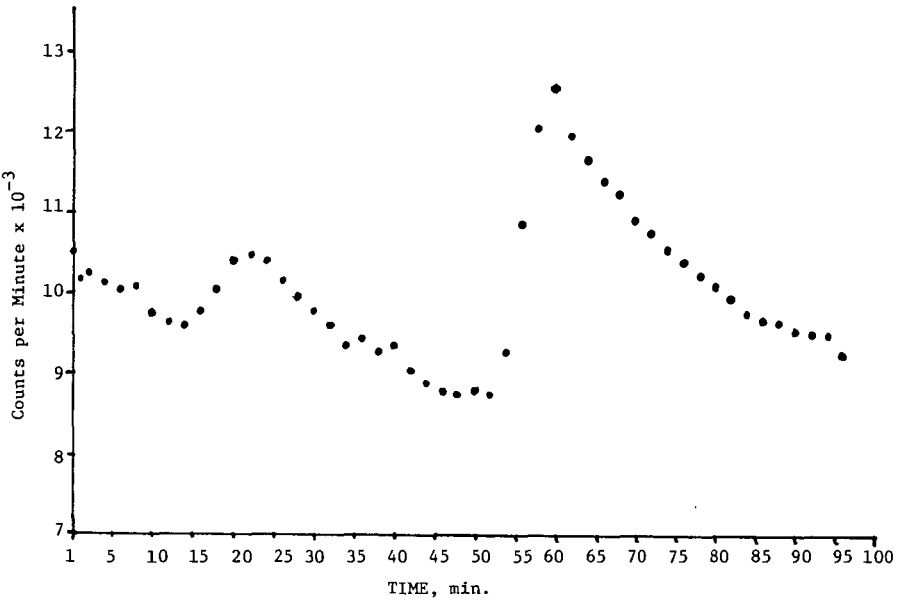

Figure 1. Luminescence on Dehydration for 87 mg Low Ash Coal 20%(w/w) in H_2O

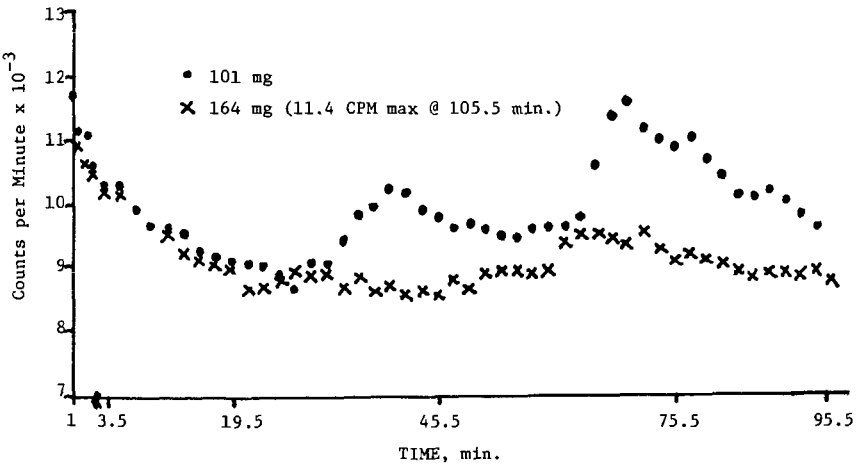

Figure 2. Effect of Sample Size on Luminescence of Low Ash Coal,20% in H_2O

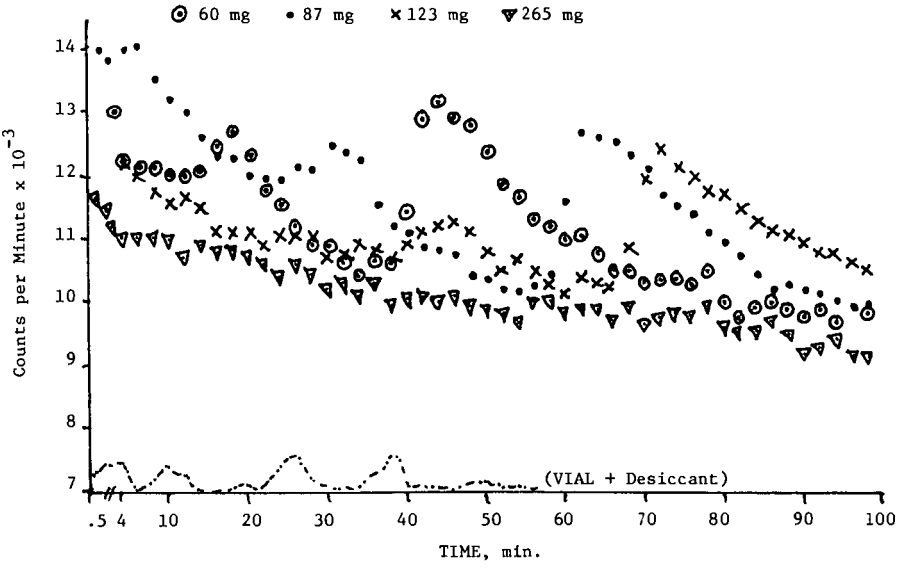

Figure 3. Effect of Sample Size on Luminescence of High Ash Coal, 20% in H_2O